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Fingerprinting coal-derived gases from the UK

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ABSTRACT

The large-scale extraction of unconventional hydrocarbons in the United States has led to fears of methane contamination of shallow groundwaters. Differentiating between the deep gas released during extraction (shale gas, coal bed methane and underground coal gasification) and natural shallow-sourced methane is imperative for the monitoring and managing of environmental risks related to the extraction process. Here, for the first time, we present measurements of the major gas, and stable and noble gas isotope composition of coal bed methane (CBM) from central Scotland and coal mine methane (CMM) from central England, UK. The molecular (C_1 / (C_2 + C_3) = 21 to 121) and stable isotope compositions ($\delta^{13}C_{CH4}$ = −39.5 to −51.1‰; δD_{CH4} = −163 to −238‰) indicate a thermogenic origin for the methane. They are distinct from the majority of shallow-sourced gases in UK. Both sample suites exhibit high He concentrations (338 to 2980 ppmv) that are considerably above atmospheric and groundwater levels. Simple modelling shows that these high ^4He concentrations cannot be solely derived from in situ production since coal deposition, and hence the majority is derived from the surrounding crust. The Scottish CBM contains a resolvable mantle He, Ne and Ar contribution that may originate from melts in the deep crust, demonstrating the UK coals have acted as a store for deep volatiles for 10s of millions of years. The high ^4He in the coal-derived gases has the potential to be used as a novel diagnostic fingerprint to track fugitive release of deep methane from future unconventional gas extraction operations in the UK.

1. Introduction

The development of horizontal drilling and hydraulic fracturing techniques has permitted the extraction of oil and gas from an array of unconventional reservoirs (e.g. Tour et al., 2010). The economic impact of unconventional shale gas exploitation in the US has been significant, and it has prompted investigation of the potential for unconventional hydrocarbons around the world. Many existing (North America, Australia) and emerging (e.g. China, Argentina, Russia, Brazil) unconventional gas reservoirs are close to potable water resources (Conti et al., 2013; Day, 2009; Mauter et al., 2014; Measham and Fleming, 2014; Vörösmarty et al., 2010), and concern has been raised over the impact of unconventional hydrocarbon exploitation, often by hydraulic fracturing, on groundwater resources (e.g. Vengosh et al., 2014). While several studies have identified deep methane in groundwater near unconventional production wells (Jackson et al., 2013a; Osborn et al., 2011), in the majority of cases this is the result of leakage from the casing of new or pre-existing wells and is not due to fractures to surface caused by the hydraulic fracturing process (Darrah et al., 2014; Molofsky et al., 2011; Molofsky et al., 2013; Warner et al., 2012).

A more rigorous assessment of the environmental effects of unconventional hydrocarbon extraction requires baseline measurement of methane levels in groundwaters prior to exploration and extraction, along with the robust methods for resolving the sources of methane already present, and distinguishing them from the exploited gas (Jackson et al., 2013b; Masters et al., 2014; Moritz et al., 2015; Vidic et al., 2013). The molecular (e.g. C_1 / (C_2 + C_3)) and stable isotopic (e.g. $\delta^{13}C_{CH4}$, δD_{CH4} or $\Delta^{13}C = \delta^{13}C_{CH4} - \delta^{13}C_{C2H6}$) composition of hydrocarbon gases can be used to differentiate between thermogenic and biogenic sources (Jackson et al., 2013a; Kornacki and McCafrey, 2011; Osborn et al., 2011; Whiticar, 1999). However, methane oxidation can change the isotopic signature of biogenic methane to make it similar to that of thermogenic methane (e.g. Molofsky et al., 2013; Moritz et al., 2015; Sherwood Lollar and Ballentine, 2009) as bacterial activity (aerobic or anaerobic) enriches the residual CH_4 in ^{13}C. Further, simple mixing between biogenic and thermogenic methane can also mask the initially diagnostic isotopic composition (e.g. Whiticar, 1999).

Trace quantities of the noble gases (He, Ne, Ar, Kr and Xe) are present in natural hydrocarbons and provide a complimentary

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fingerprinting tool that are not affected by chemical or biological processes. When combined with stable isotopes they have proved to be effective tracers of gas origin, migration and gas-fluid interactions in the crust in conventional and enhanced oil recovery hydrocarbon fields, natural CO_2 reservoirs and coal bed fields (Ballentine and O'Nions, 1994; Ballentine and Sherwood Lollar, 2002; Gilfillan et al., 2008; Gilfillan et al., 2009; Györe et al., 2015, 2017; Holland and Gilfillan, 2013; Pinti and Marty, 1995; Zhou et al., 2005). Noble gases have been used to provide a model to describe coal derived methane and groundwater interactions quantifying the water associated with gas production and the presence of the gas desorbed from the coal (Zhou et al., 2005). Recent studies have shown that noble gas isotopes can clearly distinguish between CH_4 which had migrated from overlying formations through faulty well casings, or migrated diffusively through the subsurface as a result of an underground well integrity failure (Darrah et al., 2015; Darrah et al., 2014; Wen et al., 2016).

The United Kingdom has promising shale gas and coal bed methane resources, hosted mainly in Carboniferous strata (Andrews, 2013; Creedy et al., 2001; Harvey and Gray, 2013; Jardine et al., 2009; Masters et al., 2014). Although there is a history of hydraulic fracturing of conventional hydrocarbon and water wells in the onshore UK (Cobbing and Dochartaigh, 2007; Mair et al., 2012), only the Preese Hall well (National Grid Reference: SD 37532 36,627) which directly targets a shale formation, has been subjected to high volume hydraulic fracturing techniques to date. Despite abundant evidence that undertaken correctly, hydraulic fracturing can be employed safely (Mair et al., 2012; Masters et al., 2014; Younger, 2016), the extraction of unconventional gas remains controversial and it is essential to build trust with the public if the reserves are to be exploited. This can be partially achieved by identifying robust techniques for monitoring unplanned migration of any extraction related gases to the surrounding groundwaters. Here, we document the major gas, and the stable and noble gas isotope composition of (i) coal bed methane (CBM) from the Midland Valley of Scotland, and (ii) coal mine methane (CMM) from former coal mines in the east central England (Fig. 1). We use these measurements to place constraints on the gas origin, and to identify the presence of natural fingerprints which can be used in robust future monitoring regimes.

2. Geological setting

2.1. Airth CBM field, Central Scotland

The methane from Airth is extracted from coal seams that are part of the North-East Stirlingshire Coalfield in the Midland Valley of central Scotland (Fig. 1). The Midland Valley is a NE-SW trending terrane bounded to the north by the Highland Boundary Fault and to the south by the Southern Upland Fault, and is filled principally with Carboniferous and Devonian sediments. The targeted coal seams are in the Limestone Coal Formation of the Clackmannan Group, defined at the base by the Top Hosie Limestone and at the top by the base of the Index Limestone. The coals are 326.4 to 326 Ma in age (Upper Mississippian) (Waters et al., 2011) (Fig. 2).

Gas exploration was initiated in 1993 with the drilling of the Airth-1 well. Initially coal-bed methane production was 1.7 million m^3/day and targeted the 14 potentially productive seams that were > 0.3 m thick. Wells Airth-2 to -4 were drilled in 1996 and Airth-5 to -7 between 2004 and 2007. Dart Energy acquired the site in 2011 and a further 3 new wells and 2 side-tracks off existing wells were drilled (Masters et al., 2014 and references therein). Well depths vary between 892 m (Airth-8) and 1059 m (Airth-1) below sea level (UK Onshore Geophysical Library www.ukogl.org.uk) (Table 1). The field has been pumped for gas flow rate testing during resource appraisal, but so far has not been put into commercial production. The locations of the sampled wells are provided in Table 1.

2.2. South Yorkshire and Nottinghamshire coal mines, Central England

The South Yorkshire and Nottinghamshire coalfields are located in the north east of the Midlands region of England (Fig. 1). The coalfields are within the East Pennine coalfield, the most productive of all the UK coal measures (Allen, 1995). In contrast to the Airth CBM extraction, the Central England gases are from methane extracted from former coal mines. The majority of the mines in the region exploit the Top Hard (Barnsley) coal seam, with various other seams contributing to mined output depending on local conditions. The majority of the mined seams are Middle – Upper Pennsylvanian (313 to 304 Ma). The coals were deposited in cycles typically grading upwards from mudstone, siltstone, sandstone and coal (Waters, 2009). In general, the coals crop out in a NNW-SSE orientated band west of Doncaster and Nottingham, and dip gently to the east under Permian sandstones where they form the significant resources of the concealed coalfields.

The Prince of Wales Colliery was constructed on the site of an existing mine, on the northern edge of Pontefract in West Yorkshire. Work on the drift tunnels was started in 1975 and production commenced in the Castleford Four Foot seam in 1980 and three other seams have since been exploited. The colliery closed in 2002 after producing 1.5 million tonnes of coal per year. The Newmarket Lane Colliery, near Stanley in West Yorkshire, opened in 1837 and closed in 1983, making it one of the oldest mines in the UK. The vent well of Newmarket Lane-1 is 273 m in depth and was finished in 2008. Bevercotes Colliery in Nottinghamshire opened in 1963 and closed in 1993. Bevercotes-1 was completed in 2002 and targets the deepest seam at 700 m below sea level. The Warsop Main Colliery opened in 1893 and closed in 1989. The Warsop-1 well was completed in 2002 and is the shallowest among those sampled at 222 m. The Crown Farm (also known as Mansfield) Colliery and the Sherwood Colliery (targeted by the Old Mill Lane-1 well) located close to Mansfield. The Crown Farm Colliery opened in 1904 and closed in 1989. The well reaches 310 m below sea level and was completed in 2006. Sherwood Colliery closed in 1992 with the associated well being drilled in 2002 to a depth of 300 m. The wells have been operated by Alkane Energy UK Ltd. since drilling. Depth data in Table 1 are from the UK Onshore Geophysical Library (www.ukogl.org.uk) and completion dates are from the BGS Borehole Record, (http://www.bgs.ac.uk/data/boreholescans/home.html). The locations of the sampled wells are provided in Table 1.

3. Sampling and analytical techniques

Six wells from the Airth CBM field and six CMM wells in England were sampled for this study, with duplicates taken in all cases (Table 1). The Airth gases were collected in August 2013, following production of formation water from Airth-1 for production testing from the Airth-10 well. Airth-1 was re-sampled in August 2014 after the field had been shut-in for a year. CMM samples from England were collected in July 2014. All samples were collected in Cu-tubes using the method described in Györe et al. (2015). Samples from Scotland were analysed in two batches in January–February 2015 and in May–July 2015. In addition, tubes from the Airth-1 2014 well was analysed four times between 2 and 303 days after sampling. The England gases were analysed in March 2016.

Major gas analysis was carried out at the University of Edinburgh. Gas from the Cu tube was expanded into an evacuated all-metal line and aliquots of gas were taken by a syringe via a silicone septum. Gas was injected manually into a Perkin-Elmer AutoSystem XL gas chromatograph (GC) via a 30 m long and 0.53 mm internal diameter Sigma-Aldrich Carboxen 1010 PLOT column using helium carrier gas. A thermal conductivity detector was used for nitrogen and oxygen detection, whereas all other species were detected on a flame ionisation detector. The GC was programmed for a ramp of 40 °C for 7 min to allow resolution between O_2 and N_2, then 30 °C/min ramp up to 250 °C for heavier components. The system was calibrated with gas mixtures

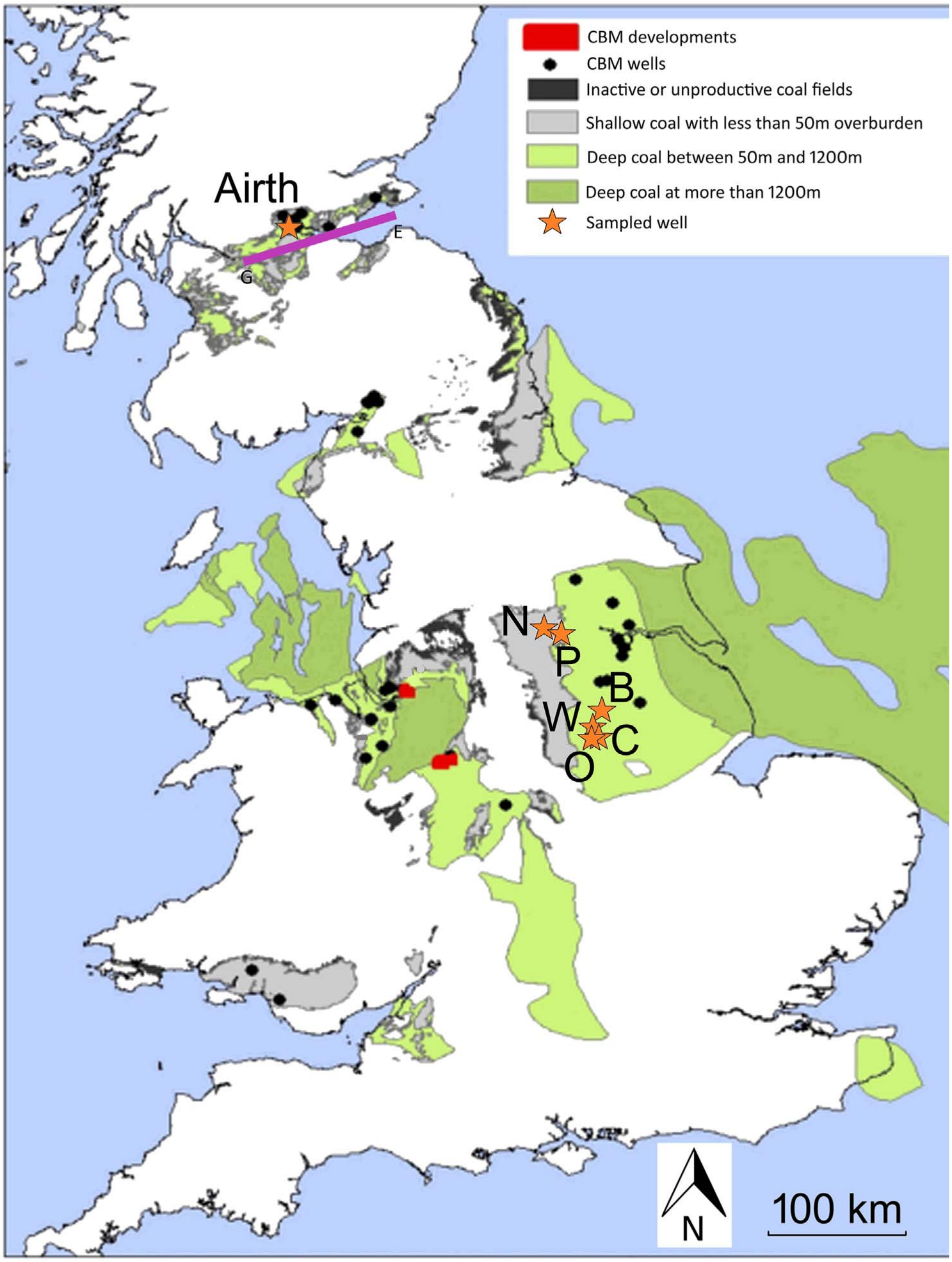

Fig. 1. The coal bed methane resources in the United Kingdom and the location of sampled wells. N: Newmarket Lane-1, P: Prince of Wales, B: Bevercotes, W: Warsop, O: Old Mill Lane, C: Crown Farm. Redrawn after Harvey and Gray (2013). The line between 'G' and 'E' is the cross section shown in Fig. 2.

produced by CalGaz Ltd. Reproducibility (1σ) of the CO_2/CH_4 and C_1 / (C_2 + C_3) ratio was ~0.5% and 0.3%, respectively.

Individual Cu tubes were crimped and half was used for stable isotope determinations. CO_2 was separated from the volatile hydrocarbons by a procedure modified slightly from Kusakabe (2005) using a liquid nitrogen-cooled isopentane trap (−160 °C). The CH_4 was combusted over a platinum catalyst at 960 °C in the presence of oxygen which was administered to the system via a septum. Flow-through was ensured by a pressure gradient between the inlet and the outlet of the furnace, generated by trapping the CO_2 and H_2O combustion products on a liquid nitrogen-cooled cold finger at the outlet. When the combustion was complete the furnace was isolated and the cold finger was heated to −80 °C by an acetone/dry ice slush trap. H_2O was retained while the CO_2 was trapped in a calibrated cold finger by liquid nitrogen. The isopentane trap was heated up to ~−80 °C, which released the CO_2 and it was trapped in a cold finger by liquid nitrogen. The isotopic composition of CO_2 (both, original and derived from CH_4) was determined on a VG SIRA II dual inlet isotope ratio mass spectrometer at SUERC (Dunbar et al., 2016), relative to V-PDB international standard (Coplen, 1994; Craig, 1957). The finger containing the H_2O (derived from CH_4) was attached to a manifold where it was vaporized by heating. The hydrogen from the water vapour was reduced in a chromium furnace at 800 °C then admitted into a VG Optima dual inlet isotope ratio mass spectrometer (Donnelly et al., 2001). δD values are given relative to V-SMOW (Gonfiantini, 1984). Experimental uncertainties (1σ) of $\delta^{13}C$ and δD determinations are 0.1‰ and 3‰, respectively.

For noble gas isotope analysis, the gas from a single Cu tube was expanded into a purpose built high vacuum system, purified by a titanium sublimation pump run sequentially between ~900 °C and room temperature and series of Zr-Al alloy getters operating at 250 °C. This pre-cleaned gas was then stored in an expansion bottle on the line, fitted with a double valve pipette for online subsampling. Full details of gas purification are reported by Györe et al. (2015). Aliquots of the stored gas were further purified by Zr-Al alloy getters, then the individual noble gases were cryogenically separated and He, Ne and Ar analysed using a MAP 215–50 mass spectrometer in static mode (Codilean et al., 2008; Williams et al., 2005). Mass fractionation,

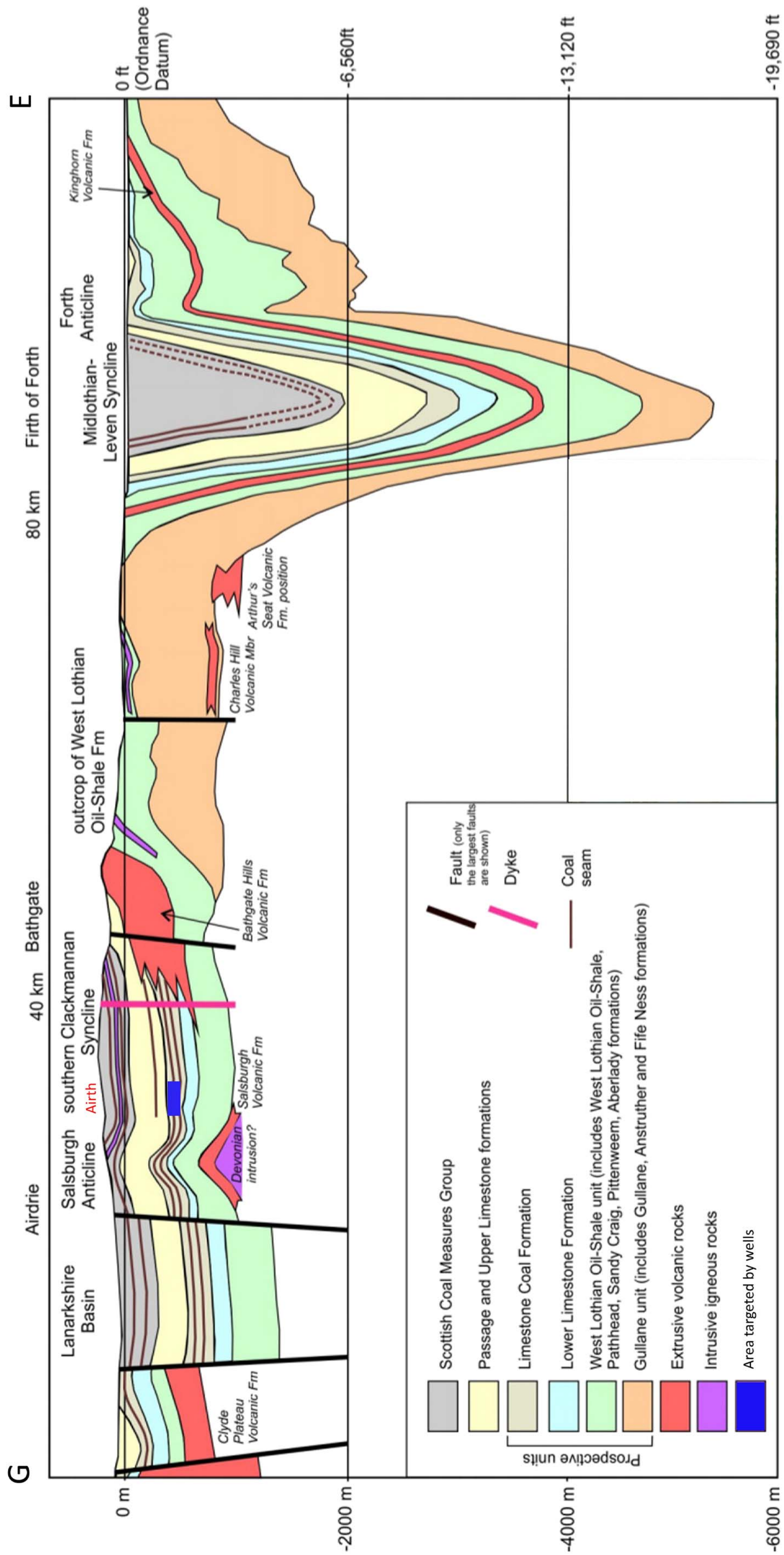

Fig. 2. Geological cross section of the Midland Valley of Scotland. Redrawn after Monaghan (2014). The location of the section can be seen in Fig. 1.

Table 1
Major gas and stable isotope composition of coal seam methane from UK.

Well	Coal field	Longitude	Latitude	Depth m	CH_4/CO_2	$C_1/(C_2 + C_3)$	$\delta^{13}C_{CO2}$ ‰ PDB	$\delta^{13}C_{CH4}$ ‰ PDB	δD_{CH4} ‰ VSMOW
Central Scotland									
Airth-1 (2013)	NE Stirlingshire	− 3.788611	56.049217	1059	–	75	–	− 40.2	− 220
Airth-1 (2014)	NE Stirlingshire	− 3.788611	56.049217	1059	–	100		− 39.5	− 163
Airth-5	NE Stirlingshire	− 3.787568	56.053725	1000	–		–	–	–
Airth-6	NE Stirlingshire	− 3.802909	56.045252	1031	–	–75	–	− 43.5	–
Airth-8	NE Stirlingshire	− 3.802799	56.045290	892	–		–	− 41.8	− 188
Airth-10	NE Stirlingshire	− 3.788119	56.048981	976	–	121	–	− 40.4	− 193
Airth-12	NE Stirlingshire	− 3.781894	56.049439	921	–		–	–	–
Central England									
Old Mill Lane-1	Nottinghamshire	− 1.183807	53.152679	300	4.4	30	–	− 50.4	− 238
Prince of Wales	South Yorkshire	− 1.312755	53.697425	500	43	69	− 24.5	− 49.6	− 233
Warsop-1	Nottinghamshire	− 1.176469	53.207939	222	26	21	− 7.9	− 51.1	− 230
Crown Farm-1	Nottinghamshire	− 1.149453	53.149176	310	2.5	40	− 11.2	− 48.8	− 211
Bevercotes-1	Nottinghamshire	− 0.958815	53.262545	700	9.1	20	–	− 46.5	− 219
Newmarket Lane-1	South Yorkshire	− 1.449143	53.725464	273	7.5	35	− 13.8	− 47.4	− 223

C_2 and C_3 are saturated hydrocarbons only.
1σ relative standard deviations of CH_4/CO_2 values are 0.5% and of $C_1 / (C_2 + C_3)$ values are 0.3%. 1σ standard deviation of $\delta^{13}C_{CO2\,\&\,CH4}$ is 0.3‰ and of δD_{CH4} is 3‰. Uncertainties include the external reproducibility of the calibration material and blanks.
Well locations are after the UK Onshore Geophysical Library: http://ukogl.org.uk/; Datum: WGS84.

sensitivity and the reproducibility of the analysis were determined by repeated analysis of HESJ international standard (Matsuda et al., 2002) for He, and air for Ne and Ar.

4. Results

4.1. Major gas and stable isotope composition

4.1.1. Airth CBM field

The gases are dominantly methane; $C_1 / (C_2 + C_3)$ varies between 75 and 121, and CO_2 concentrations are < 0.1%. The C and H isotopic compositions of the CH_4 exhibit narrow ranges ($\delta^{13}C_{CH4} = -39.5$ to -41.8‰; $\delta D_{CH4} = -163$ to -220‰) that are typical of thermogenic methane (Table 1, Figs. 3 & 4). They overlap with the isotopic composition of methane previously measured from North Sea gas field samples (Hitchman et al., 1989).

4.1.2. Central England CMM field

Unlike the CBM from Airth, these gases are not pure methane; CH_4/CO_2 varies from 2.5 (Crown Farm-1) to 43 (Prince of Wales) and $C_1 / (C_2 + C_3)$ range between 20 and 69. The C and H isotopic composition of CH_4 ($\delta^{13}C_{CH4}$–46.5 to -51.1‰; $\delta D_{CH4} = -211$ to -238‰) show a larger range than the CBM, but are also indicative of thermogenic sources (Figs. 3 & 4). The C and H isotopes overlap the field of UK coals (Hitchman et al., 1989). There is no significant relationship between the isotope and major gas composition. $\delta^{13}C$ values (-7.9 to -24.5‰) have been measured in CO_2 from 4 of the 6 CMM samples. All are heavier than the $\delta^{13}C_{CH4}$ from the same sample, indicating that the CO_2 either originates from oxidation of organic material alone or with an additional contribution of atmospheric CO_2 (see Affek and Yakir, 2014; Whiticar, 1999).

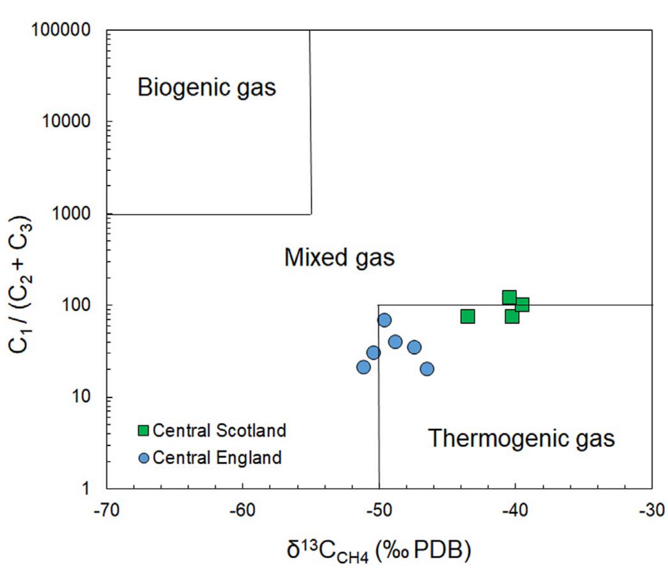

Fig. 3. The 'Bernard plot' of molecular and C isotope composition of coal-derived gases from the UK. Both central England and central Scotland gases are of thermogenic origin. Redrawn after Hachikubo et al. (2015).

4.2. Noble gases

4.2.1. Airth CBM field

Noble gas concentrations and isotopic ratios are shown in Table 2. ^4He concentrations range from 1105 ± 48 to 2984 ± 145 ppmv (Fig. 5A). $^4He/^{20}Ne$ ratios (12,931 ± 674 to 28,255 ± 1357) are significantly higher than the atmospheric value and rule out atmosphere as a significant source of the He in the gases (Fig. 5B). $^3He/^4He$ ratios vary between 0.172 and 0.187 R_A, where R_A is the atmospheric ratio of 1.399×10^{-6} (Mamyrin et al., 1970). The values are notably higher than the average $^3He/^4He$ of continental crust of 0.02 R_A (Andrews, 1985).

The concentration of Ne ranges from 0.042 ± 0.0009 to 0.354 ± 0.008 ppmv. $^{20}Ne/^{22}Ne$ vary between 10.04 ± 0.09 and 9.69 ± 0.11, while all $^{21}Ne/^{22}Ne$ (0.0330 to 0.0439) are significantly higher than the atmospheric value (0.0285) (Fig. 6). The isotopic composition of He and Ne identifies a small resolvable mantle contribution in addition to the crustal radiogenic contribution (Ballentine and O'Nions, 1991). If the mantle He is typical of the sub-continental lithosphere ($^3He/^4He = 6.1$ R_A; Gautheron and Moreira, 2002) ~2.8% of He in each well has a magmatic origin. If the mantle noble gases were derived from the proto-Iceland plume source that is known to have influenced early Tertiary volcanism in western Scotland ($^3He/^4He = 50$ R_A; Stuart et al., 2003) it would comprise 0.3% of the total He in the CBM.

$^{40}Ar/^{36}Ar$ show large variation (371 ± 4 to 1032 ± 6). All samples are notably higher than the air value of 298.6 (Mark et al., 2011) indicating the presence of radiogenic ^{40}Ar in the fluids. $^{38}Ar/^{36}Ar$ are identical to the atmospheric value of 0.189. Ar concentrations range from 71.9 ± 1.4 ppmv to 295.9 ± 5.6 ppmv, respectively, which is

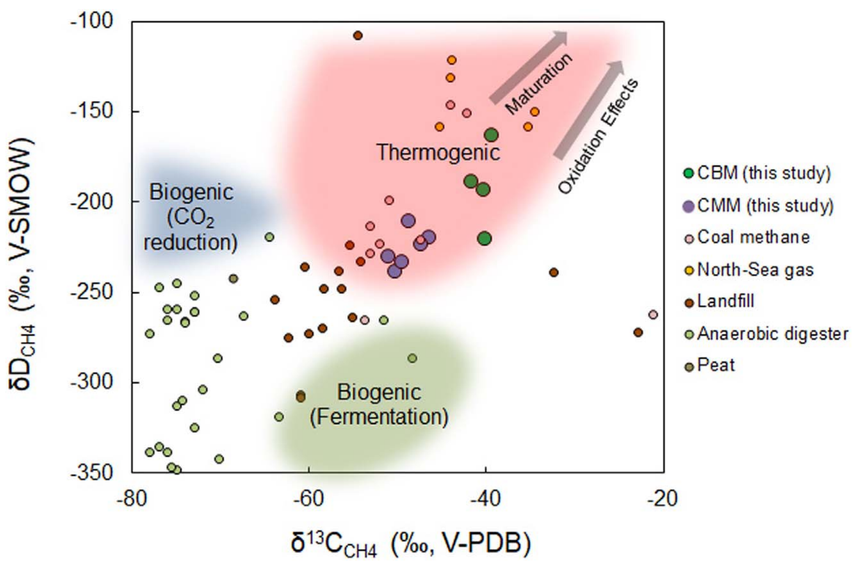

Fig. 4. The isotopic composition of coal seam methane, along with other methane-rich gases from UK. All data are from Hitchman et al. (1989) & Waldron et al. (1999). The plot is after Schoell (1980).

consistent with varying amount of air derived gases being present in these samples. $^{40}Ar^*/^4He$ (where $^{40}Ar^*$ is non-atmospheric Ar) of Airth-5 is 0.019 ± 0.0007. This value is an order of magnitude lower than crust-derived radiogenic noble gases (0.2; Torgersen et al., 1989 and is consistent with the preferential loss of He from crustal minerals by diffusion and recoil (e.g. Ballentine and Burnard, 2002).

4.2.2. Central England CMM field

Helium concentrations are lower and Ne and Ar concentrations are higher than the Airth CBM (Fig. 5A & B). ^4He varies from 338 to 1094 ppm and $^3He/^4He$ ratios are an order of magnitude lower than the central Scotland gases, varying from 0.002 R_A (Newmarket Lane-1) to 0.043 R_A (Crown Farm-1). These are typical of crustal radiogenic He and indicate that there is no contribution of mantle-derived He.

The $^{20}Ne/^{22}Ne$ ratios overlap air within 1σ uncertainty apart from the Newmarket Lane-1 (9.62 ± 0.06) and Prince of Wales (9.64 ± 0.05) mines. $^{21}Ne/^{22}Ne$ values in two samples (Bevercotes-1: 0.0316 ± 0.0003 & Prince of Wales: 0.0305 ± 0.0003) are significantly different from those of the atmosphere. The lowest $^{21}Ne/^{22}Ne$ (0.0280 ± 0.0003, Crown Farm-1) is associated with the highest $^3He/^4He$. Four samples plot on the mass fractionation line, while the remaining two can be explained by the mixture of isotopically fractionated air and crust-derived nucleogenic Ne in the sample (Fig. 6). Isotopic fractionation of Ne isotopes from natural gases has been observed elsewhere and can be explained by the differences in molecular diffusivities of the different Ne isotopes (e.g. Peeters et al., 2002; Zhou et al., 2005). It is also possible that small variation of the O/F ratio has resulted the observed isotopic ratios in those samples (e.g. Kennedy et al., 1990).

$^{40}Ar/^{36}Ar$ are generally lower than in the Airth CBM. Bevercotes-1 shows the highest $^{40}Ar/^{36}Ar$ (367 ± 1), while all others exhibit values close to the air ratio. This is indicative of small amount of radiogenic Ar. The dominance of air-derived Ne and Ar in these gases probably reflects varying amounts of air in the sample. $^{40}Ar^*/^4He$ are varying from 0.018 (Newmarket Lane-1) to 0.07 (Crown Farm-1).

5. Discussion

5.1. Source of the crustal radiogenic ^4He in CBM and CMM

Both regions exhibit high ^4He concentrations that have the potential to be a useful discriminant of deep gas in the shallow subsurface. In the CBM from central Scotland the mantle-derived He accounts for < 3% of the total, thus in both regions the ^4He is radiogenic. The ^4He likely

Table 2
Noble gas concentrations and isotopic ratios of coal bed gases from Central Scotland and Central England.

Well	$^3He/^4He$ (R/R_A)	$^{20}Ne/^{22}Ne$	$^{21}Ne/^{22}Ne$	$^{40}Ar/^{36}Ar$	$^{38}Ar/^{36}Ar$	^4He (× 10^{-3})	^{20}Ne (× 10^{-7})	^{40}Ar (× 10^{-3})	$^{40}Ar^*/^4He$
Central Scotland									
Airth-1 (2013)	0.178 (4)	10.04 (4)	0.0439 (6)	1015 (6)	0.191 (2)	1.18 (5)	0.416 (9)	0.090 (2)	0.054 (3)
Airth-1 (2014)	0.179 (3)	9.96 (4)	0.0401 (6)	879 (5)	0.187 (3)	1.29 (7)	0.51 (3)	0.071 (2)	0.036 (3)
Airth-5	0.184 (7)	9.86 (4)	0.0330 (4)	371 (4)	0.192 (2)	2.98 (15)	3.54 (8)	0.296 (6)	0.019 (3)
Airth-6	0.172 (4)	9.82 (4)	0.0415 (5)	779 (5)	0.191 (1)	2.10 (10)	0.97 (2)	0.149 (3)	0.043 (3)
Airth-8	0.174 (2)	9.69 (5)	0.0393 (6)	844 (5)	0.189 (2)	2.00 (9)	0.89 (2)	0.149 (3)	0.048 (3)
Airth-10	0.180 (4)	9.71 (5)	0.0438 (8)	1032 (6)	0.189 (2)	1.11 (5)	0.49 (1)	0.092 (2)	0.059 (3)
Airth-12	0.187 (6)	10.02 (5)	0.0369 (5)	631 (4)	0.190 (2)	2.40 (10)	1.89 (4)	0.244 (5)	0.053 (3)
Central England									
Old Mill Lane-1	0.0068 (5)	9.80 (5)	0.0284 (3)	300 (1)	0.186 (3)	0.35 (2)	50.2 (3)	4.4 (2)	0.06 (70)
Prince of Wales	0.0268 (6)	9.64 (5)	0.0305 (3)	327 (1)	0.187 (3)	1.10 (5)	2.4 (1)	0.31 (1)	0.02 (1)
Warsop-1	0.0267 (8)	9.75 (5)	0.0288 (3)	308 (1)	0.186 (3)	0.34 (2)	3.2 (1)	0.39 (1)	0.04 (6)
Crown Farm-1	0.0429 (9)	9.79 (5)	0.0280 (3)	300 (1)	0.186 (4)	0.35 (2)	76.9 (4)	5.4 (2)	0.07 (60)
Bevercotes-1	0.0027 (1)	9.70 (5)	0.0316 (3)	367 (1)	0.187 (3)	1.09 (5)	1.14 (5)	0.156 (6)	0.027 (5)
Newmarket Lane-1	0.0019 (1)	9.62 (6)	0.0285 (3)	303 (2)	0.192 (5)	0.80 (4)	13.3 (6)	1.05 (4)	0.018 (50)
Air	1.000 (9)	9.81 (8)	0.0285 (2)	298.6 (3)	0.1885 (3)	0.005 (0)	164.5 (4)	9.34 (1)	NA

1σ uncertainties are displayed as last significant figures in parentheses.
Noble gas concentrations are given in cm^3 STP/cm^3 and standard conditions are after Ozima and Podosek (2002) (p = 0.101 MPa, T = 0 °C).
Air composition is after Eberhardt et al. (1965); Honda et al. (2015); Mamyrin et al. (1970); Mark et al. (2011); Ozima and Podosek (2002).

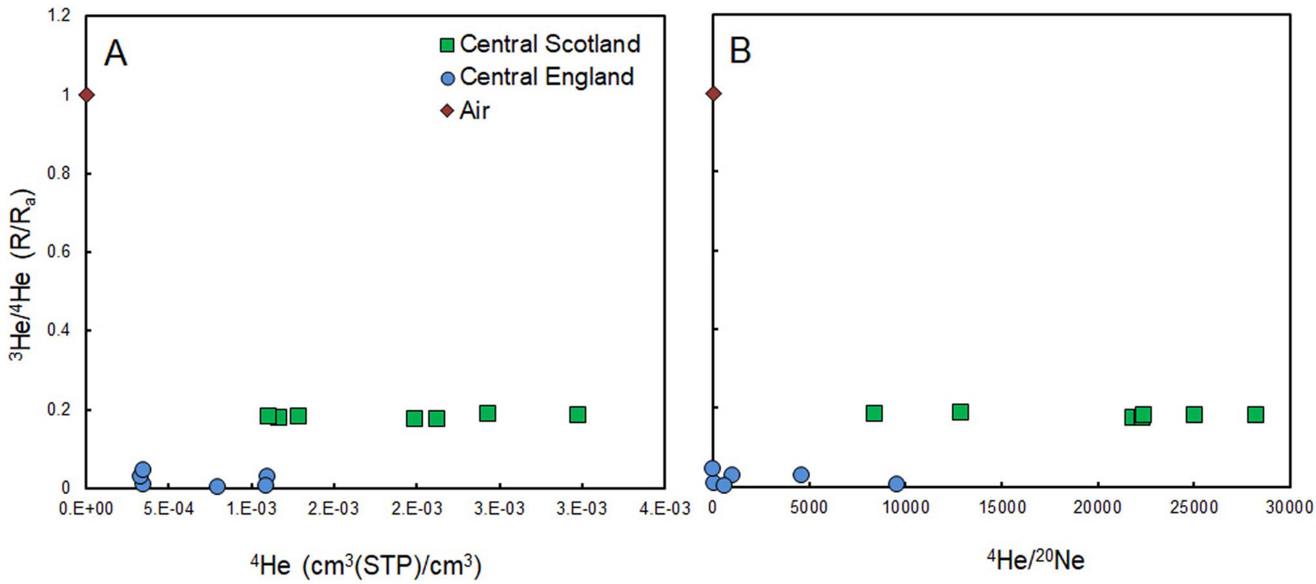

Fig. 5. Plot of $^{3}He/^{4}He$ vs. ^{4}He concentration (A) and $^{3}He/^{4}He$ vs. $^{4}He/^{20}Ne$ of well gases. Data illustrate that all coal gas samples have significantly more radiogenic $^{3}He/^{4}He$ ratios than air, and higher ^{4}He and $^{4}He/^{20}Ne$ ratios compared to those of atmospheric air.

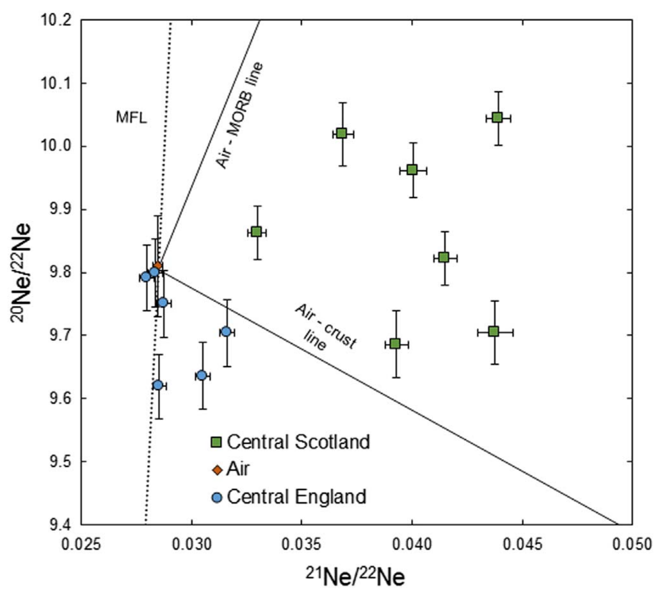

Fig. 6. The isotopic composition of Ne of coal seam methane from central England and central Scotland. Samples from central Scotland have a small contribution of mantle-sourced Ne. Samples from central England contains fractionated air mixed with crust-derived Ne at different degrees. MFL: mass fractionation line. Uncertainties are 1σ. Air is after Honda et al. (2015), MORB is after Holland and Ballentine (2006), crust end-member is after Ballentine and Burnard (2002).

originates from two sources; i) radiogenic ^{4}He produced in the coal; and/or ii) incorporation of the crustal flux of ^{4}He.

Using the age of the Airth coal beds (~320 Ma) and U and Th concentration of Scottish coals of similar age (1.6 ± 0.4 and 4.6 ± 4.2 mg/kg coal, respectively; Hamilton, 1974; Salmon et al., 1984 the in situ ^{4}He concentration ranges from 48.7 to 156.8 cm^3 STP/t coal (Vermeesch, 2008). Assuming all the in situ ^{4}He is in the gas phase, the concentration of ^{4}He in the sampled gases can be determined using estimates of methane concentration in the coal. CH_4 in Scottish coals can be as low as 0.2 m^3/t (Creedy, 1991) but concentrations of 8–10 m^3/t are reported from well Airth-1 (Bacon, 1995). Using Airth methane values, we calculate in situ ^{4}He concentrations of up to 19.6 ppmv (156.8 cm^3 ^{4}He/8 m^3 CH_4). This is more than two orders of magnitude lower than the highest measured He concentration (2984 ppmv) and suggests that the majority of the He in the gas phase originates from the local crust.

The in situ radiogenic He production in the central England CMM gases can be calculated using the same method. Using the U and Th content of coal seams targeted by the abandoned mines (1.6 ± 0.7 and 4.7 ± 1.7 mg/kg coal respectively; Hamilton, 1974) and a mean coal age of 308.5 Ma, the maximum ^{4}He concentration is 141.7 cm^3 STP/t coal. This is similar to that of the Airth coals. Methane concentrations in the Yorkshire and Nottinghamshire coals are 3.8 and 4.1 m^3/t coal, respectively (Creedy, 1991). This would generate ^{4}He concentrations up to 44.3 ppmv. Assuming all the in situ He is now in the gas phase the in situ production can account for < 14% of the measured ^{4}He. As with the Airth CBM gases, it is clear that the bulk of the ^{4}He contained in the CMM samples also originates from a source external to the coal seams.

Most natural gas reservoirs have He concentrations that are higher than can be produced by in situ radiogenic production (e.g. Kipfer et al., 2002). A 'steady state' crustal degassing model has been developed to account for the high ^{4}He content of groundwaters (e.g. Torgersen et al., 1989) and natural gases (e.g. Sano et al., 1986). This is most readily understood to result from grain boundary diffusion of radiogenic He up through the crust. It is also a possibility that thermotectonic events result in episodic release of ^{4}He from the deep crust (e.g. Ballentine and Burnard, 2002). The concentration of He in the Carboniferous coal seam gases studied here are similar to those recorded for natural gas accumulations in other Palaeozoic strata (Fig. 7). For instance, Carboniferous coal seams in the Silesian and Lublin basins of Poland, located at similar depths to those of the CMM samples, have similarly high ^{4}He contents (e.g. Kotarba, 2001; Kotarba and Rice, 2001). These are as high as He concentrations in conventional gas fields in the same age reservoir rocks (Ballentine and Sherwood Lollar, 2002; Hiyagon and Kennedy, 1992; Kotarba et al., 2014). The high ^{4}He concentration we observe appears to be independent of whether the gas is a mine vent gas (England) or an extensively pumped coal seam (Scotland). As all prospective onshore UK unconventional reservoirs are Palaeozoic in age, for example the Bowland Shale (Andrews, 2013), they can be expected to exhibit similar high ^{4}He content to the gases reported here.

5.2. Origin of mantle-derived noble gases in Central Scotland CBM

The He, Ne and Ar isotope systematics (Figs. 5–6) of the Airth CBM gases indicate that a small but significant contribution of mantle-

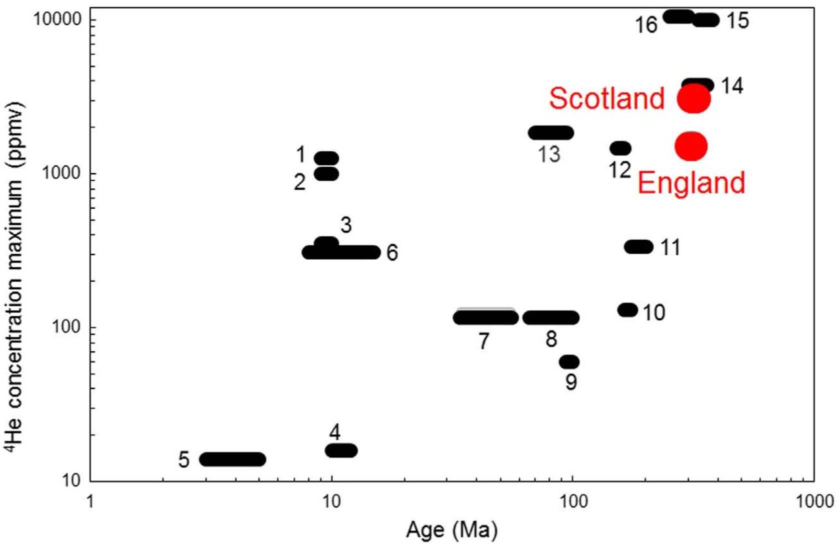

Fig. 7. Maximum ^{4}He concentration of hydrocarbon fields plotted against their age. ‰ δ Mesozoic–Cenozoic reservoirs have variable He contents, likely dependant on the age of the basement and distance from the reservoir. Paleozoic reservoir gases all appear to have high He concentrations. Most UK shale and coal gas reserves are hosted in Paleozoic reservoirs therefore high ^{4}He is expected. 1–3: Pannonian Basin (Ballentine et al., 1991; Cornides et al., 1986; Sherwood Lollar et al., 1994), 4: Elk Hills oil field (Torgersen and Kennedy, 1999), 5: Dosso Degli Angeli field (Elliot et al., 1993), 6: Vienna Basin (Ballentine and O'Nions, 1991), 7: Sacramento and N San Joaquin basins (Jenden et al., 1988; Poreda et al., 1986), 8: San Juan Basin (Zhou et al., 2005), 9: Mediterranean Coastal Plain (Bosch and Mazor, 1988), 10: Magnus field (Ballentine et al., 1996), 11: Potiguar Basin (Prinzhofer et al., 2010), 12: Ukrainian and Polish Flysch Carpathians (Kotarba and Nagao, 2008), 13: Songliao Basin (Xu et al., 1995), 14: Polish Basin (Kotarba et al., 2014), 15: Alberta gas fields (Hiyagon and Kennedy, 1992), 16: Hugoton Panhandle giant gas field (Ballentine and Sherwood Lollar, 2002).

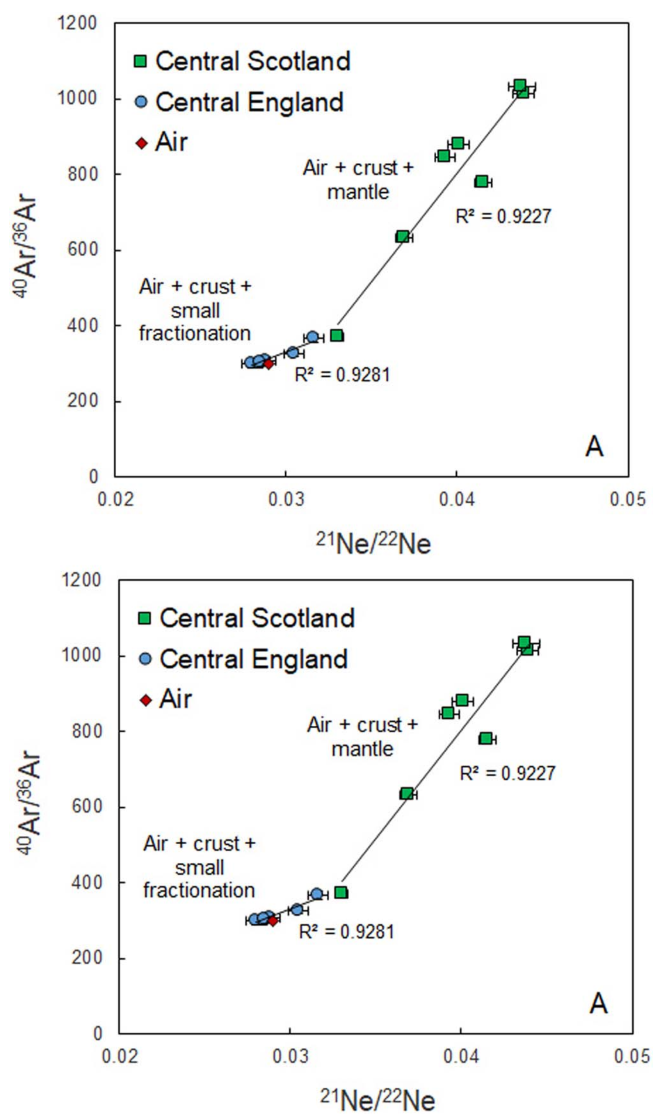

Fig. 8. Plot of ^{40}Ar/^{36}Ar vs. ^{21}Ne/^{22}Ne (A) and ^{40}Ar/^{36}Ar vs. ^{4}He/^{36}Ar (B) of gases from Central England and Central Scotland. Mixing between atmospheric end-member (Central England) and a mantle and atmospheric end-member (Central Scotland) is observed in both Fig. 1 sigma uncertainties are smaller than symbols.

derived volatiles is trapped within the coals. This is further highlighted in plots of ^{40}Ar/^{36}Ar vs. ^{21}Ne/^{22}Ne (Fig. 8A) and ^{40}Ar/^{36}Ar vs. ^{4}He/^{36}Ar (Fig. 8B) which demonstrates the difference in the non-atmospheric gases from the two regions. In both figures the CMM from northern England shows a mixing between air and a ^{21}Ne-, ^{40}Ar- and ^{4}He-rich gas that is consistent with crust-derived noble gases. In contrast, the Scottish dataset clearly shows the presence of a mantle end-member as the mixing line does not pass through the atmospheric ^{40}Ar/^{36}Ar end member. In both cases the sharp increase of ^{40}Ar/^{21}Ne (A) and ^{40}Ar/^{4}He (B) relative to the English dataset is consistent with the changing production of ^{40}Ar, ^{21}Ne and ^{4}He from the Upper to the Lower crust (Ballentine and Burnard, 2002).

This is the first record of mantle-derived volatiles in onshore UK gases (Oxburgh et al., 1986) and is rather unexpected given the absence of basaltic magmatism or rifting in the last 60 million years. The region has experienced two periods of magmatism since coal formation that could be the source for the mantle-derived volatiles; widespread melting of the sub-continental lithosphere during rifting in the Late Carboniferous-Early Permian (Wilson et al., 2004) and melts of upwelling proto-Iceland plume mantle in the early Cenozoic (Saunders et al., 1997).

The deposition of coals in the Upper Mississippian coincided with extensive basaltic volcanism throughout the Midland Valley of Scotland, that continued until Early Permian times. This was accompanied by the intrusion of thick, widespread sill-complexes during the Lower-Middle Pennsylvanian by a widespread suite of tholeiitic sills and dykes. At this time, the Midland Valley graben had developed into an intra-continental rift, where lithospheric stretching had led to rifting and increased thermal gradients with consequent mantle melting.

The arrival of the proto-Iceland plume beneath the North Atlantic resulted in extensive basaltic magmatism in western Scotland and Northern Ireland at 58–61 Ma. In contrast to the Permo-Carboniferous magmatism, there is little sign of early Tertiary intrusive or extrusive volcanic rocks in central Scotland. The Mull dyke swarm lies ~50 km south of Airth and displays small basaltic fissures, but there is little evidence that the deep crust below the Midland Valley received a significant thickness of melt (Fig. 2).

The *E*-W trending Ochil Fault lies 12 km to the north of the Airth CBM field and cuts the Carboniferous coals of the Midland Valley. It has a vertical throw of ~4 km and is seismically active (Rippon et al., 1996) and may be a plausible conduit for the mobilisation of mantle volatiles exsolved from mantle melts that underplated the deep crust in the early Cenozoic. The main fault and its splays host several precious metal ore deposits and uraniferous bitumens derived from down-thrown

Carboniferous sediments (Gallagher et al., 1971; Robinson et al., 1989). It is highly likely that the fault has been a conduit for deep (magmatic) fluids throughout the late Palaeozoic and Mesozoic.

5.3. Fingerprinting coal derived methane occurrences in onshore UK fields

The major gas and stable isotopic composition of CH_4 of both the CBM and CMM gases clearly indicate a thermogenic source (Figs. 3 & 4), suggesting that this may be widespread in UK coals. $\delta^{13}C_{CH4}$ and δD_{CH4} of CBM and CMM overlap UK coal gases, particularly with landfill gases, and North Sea natural gases respectively (Fig. 4). For the most part they are distinct from shallow-sourced methane, e.g. peat (Fig. 4), however there is significant overlap between coal-derived gases from this study and the field defined by landfill methane (Fig. 4), confirming that the C and H isotopes can be ambiguous as source tracers.

The diagnostic feature of the noble gases in the coal-derived gas from both regions in UK is the high ^4He concentrations. They are significantly higher than expected for shallow sourced methane, and recently recharged groundwaters, which contain He in atmosphere concentrations (~5 ppmv). ^4He has previously been used to identify the natural migration of CO_2 to groundwaters in Arizona (Gilfillan et al., 2011), the migration of hydrocarbons to the shallow subsurface in Wyoming (Ballentine and Mackintosh, 2012) and in allegations of CO_2 contamination in Saskatchewan (Gilfillan and Haszeldine, 2011; Gilfillan et al., 2017). When combined with ^{20}Ne and ^{36}Ar, He has been used to distinguish CH_4 leaking through faulty well casings (Darrah et al., 2014), identify the source of naturally-occurring methane in groundwaters in the northern Appalachain basin (Darrah et al., 2015), and show that high CH_4 in groundwaters in Texas are unrelated to gas extraction (Wen et al., 2016).

The high ^4He concentration in coal seam-derived CH_4 has potential as a diagnostic fingerprint to identify any unplanned gas migration from deep to the shallow subsurface. An array of portable, high sensitivity He detector technologies are commercially available which allows precise determination of sub-atmospheric He concentrations. This technology could be used for real time monitoring of natural gas release, and to record fugitive emissions around sites of gas extraction. Membrane inlet mass spectrometers have been developed for continuous measurement of dissolved noble gas concentrations in groundwaters (Mächler et al., 2012). They could be deployed in wells to monitor the He concentrations prior to and during drilling and hydraulic fracturing to provide early warning of deep gas ingress into groundwater. Mature hydrocarbon-bearing shales underlie the Carboniferous coals in many parts of the UK and many hold economic reserves of both CH_4 and potentially ^4He. Establishing infrastructure for real time monitoring of He in gas and waters in the UK offers a robust technique for monitoring for unplanned migration of methane from unconventional gas extraction related gases to the surrounding groundwaters.

6. Conclusion

In this study we show that the molecular and stable isotopic composition range of both CBM from Central Scotland, and CMM for Central England is diagnostic of a thermogenic origin for the CH_4 and other light hydrocarbon gases present. We find that he CMM samples have a significant CO_2 component, that either originates from the oxidation of organic material alone or with an additional contribution of atmospheric CO_2, whereas the CBM samples are primarily CH_4 with minor C_2 and trace C_3 hydrocarbons. Both the CBM and CMM contain significantly above atmospheric levels of ^4He. The compositions of unconventional gas reservoirs in the UK we report here show that there is great potential for the application of these tracing techniques, as the reservoirs show elevated ^4He concentrations even at relatively shallow depths. This is particularly the case in the Airth CBM field in Scotland, which shows the highest ^4He concentration measured in a shallow Paleozoic aquifer to date of up to ~3000 ppmv. There are underlying mature hydrocarbon bearing shale formations which are currently being explored for unconventional gas beneath both the Airth CBM field, in the Midland Valley of Scotland and the Central England region where CMM is being extracted. From the results of this study we expect that any gas produced from these shale formations will also exhibit high ^4He concentrations and hence real time monitoring of He in gas and waters in the UK potentially offers a robust technique for monitoring for unplanned migration of any deep sourced methane related to these activities.

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